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Thermodynamic activation and ultrasound-induced degradation dynamics of carboxymethyl cellulose (CMC)

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الديناميكا الحرارية للتنشيط وحركية التحلل المستحث بالموجات فوق الصوتية لكربوكسي ميثيل السليلوز *CMC*

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Abstract

The research determined thermodynamic activation parameters for carboxymethyl cellulose (CMC) in water-based NaCl solutions through analysis of original high-molecular-weight CMC and its low-molecular-weight counterpart which resulted from ultrasound-induced degradation. The research team measured relative viscosity (ηr) of dilute solutions by testing different solution concentrations and temperature ranges. The research findings demonstrated that viscosity values experienced substantial changes when scientists altered solution concentrations and temperature levels. Scientists used Moore's technique which Arrhenius and Eyring equations helped them transform relative viscosity data into activation parameters which included the pre-exponential factor (A) and activation enthalpy (ΔH) and activation entropy (ΔS). The three parameters showed strong dependency on polymer concentration and solution viscosity and molecular weight. The high-molecular-weight CMC showed activation enthalpy and pre-exponential factor values which were higher than low-molecular-weight CMC but its activation entropy value was lower which means it resists flow better than low-molecular-weight CMC. The ultrasound-degraded CMC demonstrated better flow properties because its energetic obstacles became less difficult to overcome. The rising temperature caused viscosity to change in a non-linear pattern which also changed the activation parameters. The research team discovered how CMC flow behavior results from enthalpic and entropic factors while they showed ultrasound degradation effects on polymer solution behavior based on temperature and polymer concentration and molecule size.

Keywords: Ultrasound degradation, Carboxymethyl cellulose, Arrhenius and Eyring parameters, Relative viscosity, Molecular weight.

الملخص

حددت الدراسة معاملات التنشيط الثرموديناميكية لكربوكسي ميثيل السليلوز (CMC) في محاليل NaCl المائية من خلال تحليل CMC الأصلي ذي الكتلة الجزيئية المرتفعة ونظيره منخفض الكتلة الجزيئية الناتج عن التحلل المستحث بالموجات فوق الصوتية. تم قياس اللزوجة النسبية (ηr) لمحاليل مخففة عند تراكيز مختلفة وعلى مدى متباين من درجات الحرارة. وأظهرت النتائج أن قيم اللزوجة تتغير بشكل ملحوظ بتغير كل من تركيز المحلول ودرجة الحرارة. استُخدمت طريقة مور، بالاقتران مع معادلتي أرهينيوس وإيرينغ، لتحويل بيانات اللزوجة النسبية إلى معاملات تنشيط كعامل ما قبل الأسّي (A) ، وإنثالبي التنشيط (ΔH)، وإنتروبي التنشيط (ΔS) ، وأظهرت هذه المعاملات اعتمادًا قويًا على تركيز البوليمر، ولزوجة المحلول، والكتلة الجزيئية. سجّل CMC ذو الكتلة الجزيئية المرتفعة قيمًا أعلى لكل من إنثالبي التنشيط وعامل ما قبل الأسّي، وقيمة أقل لإنتروبي التنشيط مقارنةً بـ CMC منخفض الكتلة الجزيئية، مما يدل على مقاومة أكبر للجريان. في المقابل، أظهر CMC المتحلل بالموجات فوق الصوتية خصائص جريان أفضل نتيجة انخفاض الحواجز الطاقية. كما أدى ارتفاع درجة الحرارة إلى تغيرات غير خطية في اللزوجة وانعكست هذه التغيرات على معاملات التنشيط. توضح الدراسة إسهام العوامل الإنثالبيّة والإنتروبيّة في سلوك جريان CMC، وتبيّن تأثير التحلل بالموجات فوق الصوتية في ديناميكية البوليمر في المحلول تبعًا لدرجة الحرارة، والتركيز، والكتلة الجزيئية.

الكلمات المفتاحية: التحلل بالموجات فوق الصوتية، الكتلة الجزيئية، اللزوجة النسبية، كربوكسي ميثيل السليلوز، معاملات أرهينيوس وإيرينغ.

1. Introduction

Analyzing the energetic aspects of viscous flow is important for the rheological characterization of natural polysaccharides in solution [1]. Eyring's theory of viscous flow considers the process as an activated rate phenomenon, offering a basis for interpreting flow behavior in terms of thermodynamic activation parameters (TAP) [2]. On this basis, Moore [3,4] applied the theory to polymer solutions and computed TAP, namely, Q_η for enthalpy flow, A_η for the pre-exponential factor, and ΔS_η for the shear flow entropy, through solution viscosity (η) and molar masses (M_η) measurements.

In industrial and biomedical fields, bioactive natural polysaccharides like carboxymethyl cellulose are extensively used in diverse chain lengths and molecular weights (large, medium, and small sizes). To satisfy such needs, linear polysaccharides are often processed to reduce molar mass by degradation, which can be biological, chemical, physical, or mechanical. Among these, ultrasonic (US) degradation has been reported as a highly effective and environmentally friendly method [5].

Importantly, the degradation induced by the US happens in a single-step manner, which aids in having control over the degradation rate during the experiments [5].

Carboxymethyl cellulose (CMC) is an anionic derivative of cellulose whose usefulness stems from biocompatibility, solubility, and electrokinetic interactions [6,7]. This facilitates application across diverse disciplines: biomedicine, food packaging, wastewater treatment, textiles, fuel cells, bioplastics, and nanocomposite systems. In the case of thin film formulation and pharmaceuticals low-viscosity CMC is preferred, while for textiles, high-viscosity formulations are used [6,7].

This study will address the impact of concentration and molar mass on the thermodynamic activation parameters of ultrasound-degraded CMC in sodium chloride solution. An oversimplification is developed for the purpose of this investigation by using relative viscosity in place of absolute or intrinsic viscosity so that the molecular energetics of viscous flow in these systems may be analyzed.

2. Materials and Methods

2.1 Materials

Carboxymethyl cellulose (CMC) powder (The chemical structure is shown in Fig. 1) was supplied by TCI Chemicals (Tokyo Chemical Industry) used without further purification and the solvent was 0.01M of NaCl. The concentration (C) of the native and different irradiated CMC solutions was 1.00 mg cm^{-3}

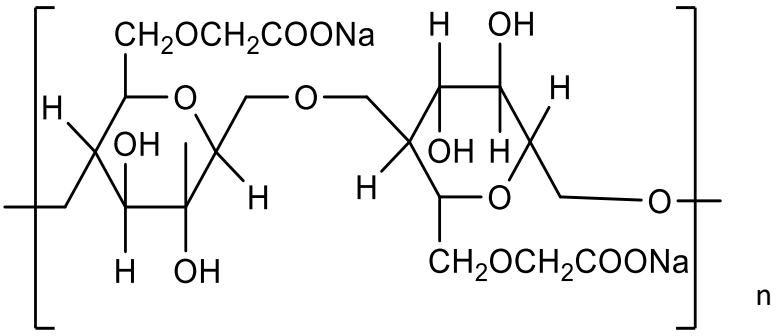


Figure 1: Monomer molecular structure of CMC

2.2 Sample Preparation and Measurement

Equal samples of mother solution were irradiated in ultrasonic bath, with an input power and frequency of 305W and 60Hz respectively (SONICA-2200 EP). The samples were irradiated with US -irradiation at the same condition for different periods of time. The experimental Set-up of US- irradiation technique has been discussed in detail in Ref. 8. The observation of change in each sample was done immediately after irradiation, and at intervals afterwards for each sample, by using Ostwald-viscometric technique [8]. In brief, the viscosity was measured in a water bath controlled to ±0.02°C.

2.3 Data Treatment

The experimental data was processed according to the relationships in Table 1, following the procedures in references [4,9].

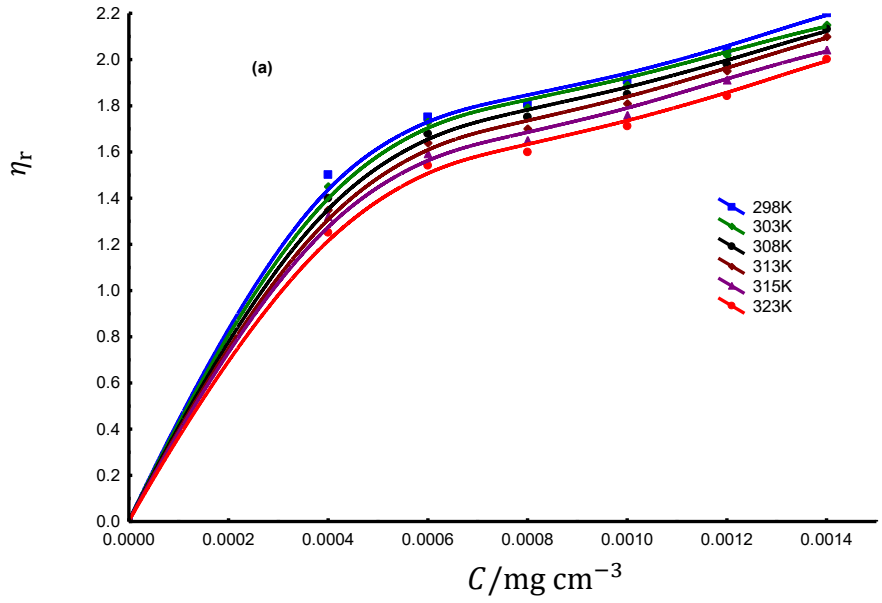
Table 1: TAP relationships of CMC

Equation	Number
$\eta_r = \eta/\eta_0$,	(1)
$\eta = t_f x \rho$	(2)
$\eta_0 = t_{f,0} x \rho_0$;	(3)
$\eta_r = \frac{\eta}{\eta_0} \sim \frac{t}{t_0}$	(4)
$\eta_r = A_{\eta,r} e^{Q_{\eta,r}/RT}$,	(5)
$A_{\eta,r} = \frac{N_A h}{V_{m,r}} e^{-\Delta S_{\eta,r}/R}$,	(6)
$V_{m,r} = \frac{V_m}{V_{m,o}} \sim 1$	(7)
$Q_\eta = Q_{\eta,r} + Q_{\eta,o}$,	(8)
$A_\eta = A_{\eta,r}\ A_{\eta,o}$,	(9)
$\Delta S_\eta = \Delta S_{\eta,r} + \Delta S_{\eta,o}$.	(10)
where the respective values of $Q_{\eta,o}$, $A_{\eta,o}$ and $\Delta S_{\eta,o}$ are: 18.73 kJ mol^{-1}, 0.582 g $m^{-1}s^{-1}$ and -83.46 J $K^{-1}mol^{-1}$.	

2. Results and Discussion

1. Viscosity relationship

According to Huggins' theory on how polymer viscosity depends on concentration [10], Figure 2a shows a nonlinear relationship for high-viscosity (HV/HM) CMC across the concentration and temperature ranges we investigated. In contrast, Figure 2b indicates also a deviation from linearity for low-viscosity (LV/LM) CMC, but at lower values of relative viscosity. This deviation may result from excluded-volume effects (solvation index) that depend on polymer concentration (C), molar mass ($M_{\eta,r}$), and temperature (T) [11,12].



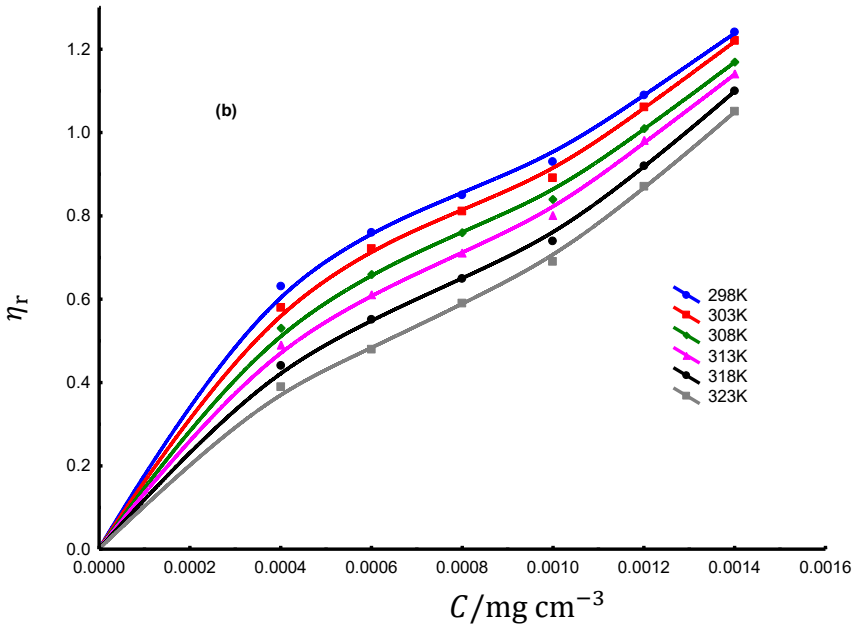


Figure 2: η_r VS C of (a) High Volume-CMC and (b) Low Volume-CMC, at different temperatures

2. Thermodynamic behavior

Figure 3 shows Arrhenius-like behavior in logarithmic form, allowing us to determine the activation energy ($Q_{\eta,r}$), pre-exponential factor ($A_{\eta,r}$) and activation entropy (ΔS_η) as noted in earlier studies [3,4,9].

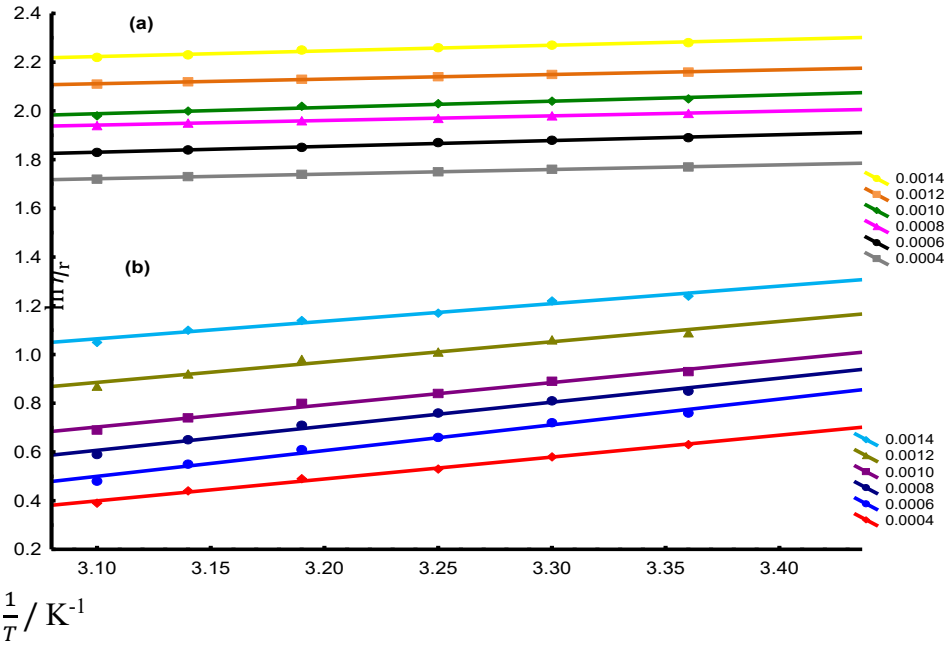
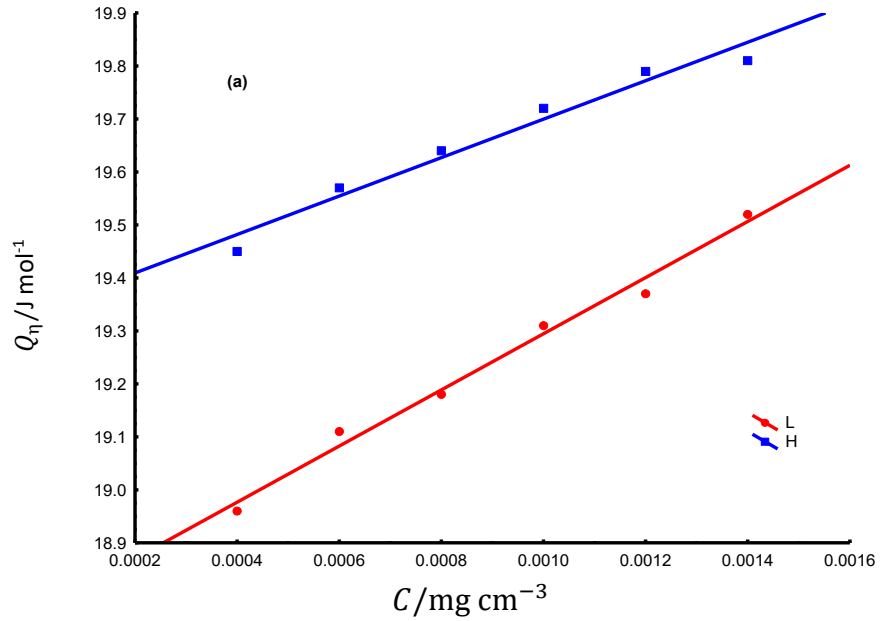


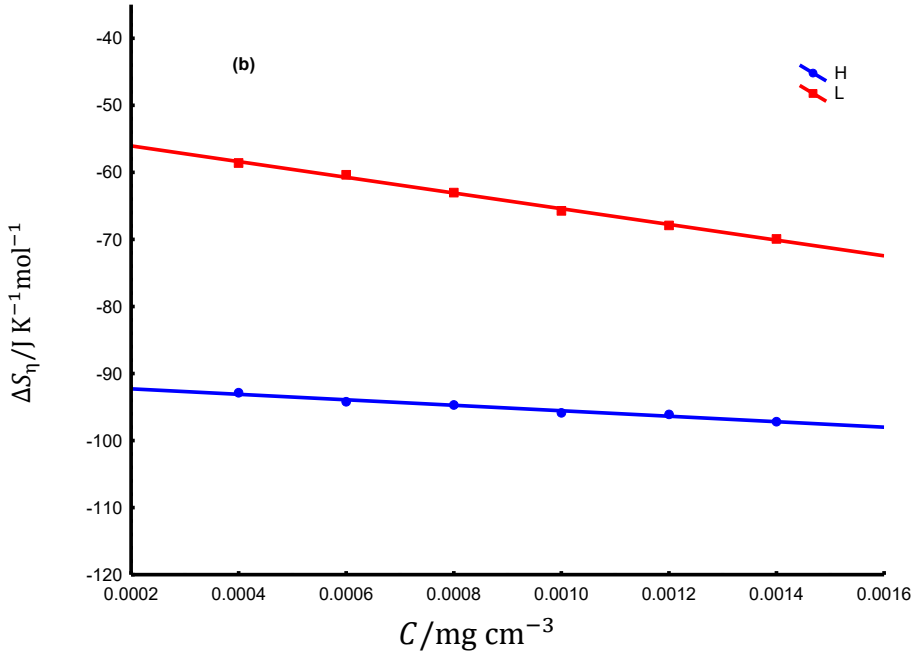
Figure 3: $\ln\eta_r$ VS T^{-1} of (a) High Volume-CMC and (b) Low Volume-CMC at different concentrations.

3. Activation parameters

We calculated the activation energy (Q_η), pre-exponential factor (A_η), and activation entropy (ΔS_η) from Equations 5–9. These values were then plotted against polymer concentration in Figure 4.

Figure 4 further illustrates that both Q_η and A_η increase with higher concentration (C) and molar mass ($M_{\eta,r}$), while ΔS_η decreases. This trend suggests that CMC chains take on a coiled shape in 0.01M aqueous NaCl solution and behave like flexible polymer chains in dilute solution [3–7].





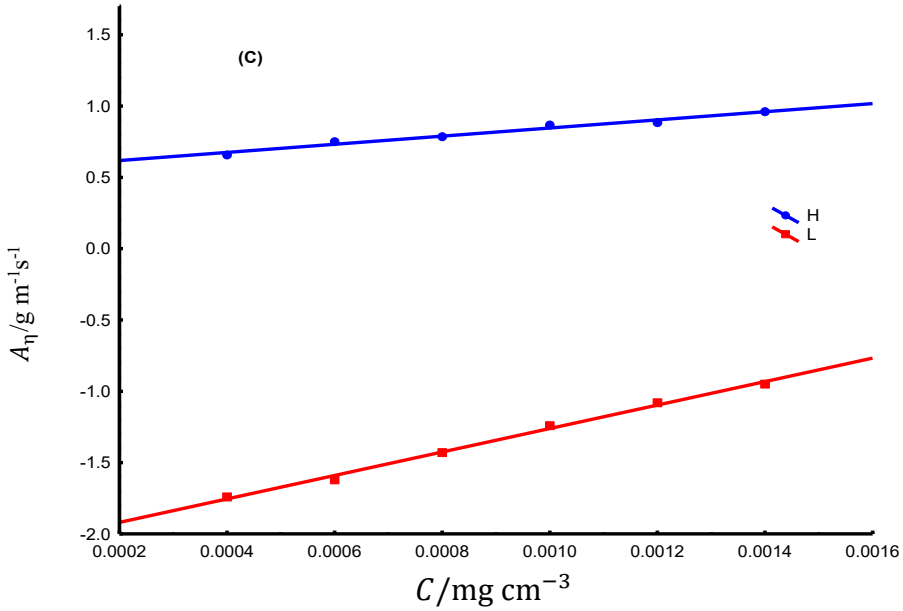


Figure 4: CMC-Concentration dependence of (a) Q_η, (b) A_η and (c) ΔS_η of (a) High Volume-CMC and (b) Low Volume-CMC

4. Conclusions

Unlike many cellulose derivatives in dilute media, the activation entropy (ΔS_η) for CMC in NaCl decreases as concentration and viscosity of polymer solution increase.

Ultrasonic degradation has been shown to be an efficient method, better than chemical or organic synthesis, for creating low-viscosity (low-molar-mass) CMC with high activation entropy and low excluded-volume effects.

For assessing thermodynamic activation parameters of cellulose derivatives, the relative viscosity method provides a valid alternative to intrinsic or solution-viscosity methods.

List of symbols and abbreviations

TAP	Thermodynamic activation parameters
Q_η	Solution apparent activation energy as well as enthalpy, η-subscript refers to the viscosity measuring method
A_η	Solution Arrhenius pre-exponential factor
ΔS_η	Solution Activation Enthalpy
η	Solution viscosity
C	Mass concentration of the polymer
M_η	Molar mass of the polymer
V_m	Molar volume of the solution
CMC	Carboxymethyl cellulose
LV	Low viscous (or viscosity)
LM	Low molar mass
HV	High viscous (or viscosity)
HM	High molar mass
VS	Versus
Aq.	Aqueous

NaCl	Sodium chloride
η_r	Relative viscosity
η_0	Solvent viscosity
t_f	Flow time of CMC solution
ρ	Density of CMC solution
$t_{f,0}$	Solvent flow time
ρ_0	Solvent density
$A_{\eta,r}$	Relative Arrhenius pre-exponential factor
$Q_{\eta,r}$	Relative apparent activation energy or enthalpy
R	Gas constant
T	Temperature
N_A	Avogadro constant
h	Planck constant
$V_{m,r}$	Relative molar volume
$\Delta S_{\eta,r}$	Relative activation entropy
V_m	Molar volume of CMC solution
$V_{m,0}$	Solvent molar volume
$A_{\eta,o}$	Solvent Arrhenius pre-exponential factor
$Q_{\eta,o}$	Solvent apparent activation energy or enthalpy
$\Delta S_{\eta,o}$	Solvent activation entropy
$M_{\eta,r}$	CMC relative molar mass

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Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.